Reconstruction and Thermal Stability of the Cubic SiC (001) Surfaces

Alessandra Catellani,[1] Giulia Galli,[2] and François Gygi[2]

[1]*CNR-MASPEC, Via Chiavari, 18/A, I-43100 Parma, Italy*

[2]*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland*

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The (001) surfaces of cubic SiC were investigated with *ab initio* molecular dynamics simulations. We show that C-terminated surfaces can have different $c(2 \times 2)$ and $p(2 \times 1)$ reconstructions, depending on preparation conditions and thermal treatment, and we suggest experimental probes to identify the various reconstructed geometries. Furthermore, we show that Si-terminated surfaces exhibit a weak $c(2 \times 1)$ reconstruction at $T = 0$, whereas above room temperature they oscillate between a dimer row and an ideal geometry below 500 K, and sample several patterns including a $c(4 \times 2)$ above 500 K. [S0031-9007(96)01930-8]

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Silicon carbide is an attractive material for high temperature microelectronic and optoelectronic devices [1] because of its wide band gap, high thermal conductivity, high hardness, and chemical inertness. Recently SiC has also emerged as a promising substrate for the growth of nitride-based devices [1,2].

In the last decade a notable effort has been devoted to the characterization of SiC surfaces, since SiC films for use in technological applications are prepared by epitaxial growth. In particular, the (001) surfaces of the cubic polytype β-SiC have been studied with a variety of experimental [3–11] and theoretical [12–15] techniques. At the end of the eighties it was established that these surfaces are terminated by only one species, and a clear assignment of different LEED patterns to either C-terminated or Si-terminated surfaces was given [3]. Nevertheless the reconstruction of the Si-terminated surface is still the subject of debate, in view of the partial disagreement between recent [10] and older [3,7] experiments. Furthermore, a long-standing controversy [4,5,12–14] about the structure of C-terminated surfaces was solved only recently [11]. At present, important problems such as the effect of preparation conditions on the surface structure and the thermal stability of the (001) surfaces are yet unsolved. These are key issues for the understanding of any growth process on SiC substrates, and represent as well fundamental problems in the physics of compound semiconductor surfaces.

In order to address these issues we performed a series of *ab initio* molecular dynamics (MD) simulations [16] of several β-SiC (001) surfaces at finite temperature. We studied various reconstruction paths of the C-terminated and Si-terminated surfaces, modeling different preparation conditions, and we identified experimental probes which could discriminate between the various reconstruction patterns. Our computations constitute the first *ab initio* analysis of the effect of preparation conditions and thermal treatment on the structure of (001) SiC surfaces.

Our calculations were carried out within the local density functional approximation (LDA). We used slabs periodically repeated in the (x,y) plane (see Fig. 1), terminated on each side by the same atomic species and followed by a vacuum region of $\simeq 8.5$ Å. In most MD simulations we used 11 layers, each containing 8 atoms. Structural optimizations at $T = 0$ were carried out with both 11 and 19 layers (152 atoms) [17]. The lateral dimensions of the supercell were 8.60×8.60 Å, corresponding to the theoretical equilibrium lattice constant of bulk SiC (4.30 Å). The experimental value is 4.36 Å. We note that the use of a symmetric slab is important to avoid spurious charge transfers and electric fields, whose effect on polar surfaces of compound materials is *a priori* unknown and might affect molecular dynamics simulations. The interaction between ionic cores and valence electrons was described by fully nonlocal pseudopotentials [18] with s and p nonlocality for Si and s-only nonlocality for C. Single particle orbitals and charge densities were expanded in plane waves with kinetic energy cutoffs (E_{cut}) of 40 and 160 Ry, respectively. We considered Bloch functions at the $\overline{\Gamma}$ point of the supercell surface Brillouin zone (SBZ); this corresponds to including the points $\overline{\Gamma}$, $\overline{M}$, $\overline{S}$, and $\overline{\Gamma}$, $\overline{J}'$ and $(\overline{J} + \overline{J}'/2)$ of the $c(2 \times 2)$ and $p(2 \times 1)$ primitive cells (001) SBZ, respectively.

C-terminated surfaces.—Experimentally, C-terminated surfaces are obtained either by ethylene decomposition on Si-terminated substrates [4,5], or by Si sublimation [3,6,9] between 1200 and 1500 K. The two techniques lead to samples characterized by different diffraction data [5] and
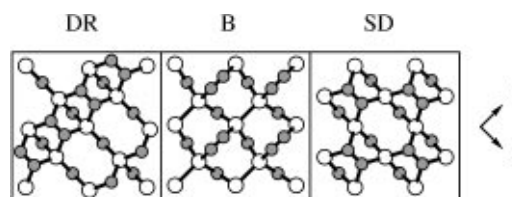

FIG. 1. Top view of the dimer row (DR), bridge (B), and staggered dimer (SD) reconstructed geometries of the C-SiC(001) surface. Three layers are shown. Black and white spheres indicate C and Si atoms. Axes are oriented as in Ref. [11]. In the three geometries dimers are not buckled.

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photoemission spectra [6,8]. We devised two series of computations to investigate the two preparation methods.

The first series of calculations concerns Si sublimation experiments. Since Si removal is expected to yield an ideally C-terminated surface [C-SiC(001)], which then reconstructs, we studied the spontaneous reconstruction of an ideally terminated C-SiC(001) and the thermal stability of its reconstructed phases. Starting from the ideal geometry vibrating at room temperature, we performed microcanonical MD simulations. Depending on the initial conditions on ionic positions and velocities, the ideal geometry transforms either into a $c(2 \times 2)$ staggered dimer (SD) pattern or into a $c(2 \times 1)$ dimer row (DR) geometry (see Fig. 1). At $T = 0$ the total energy of the DR is lower than that of the SD geometry by 0.44 eV/surface dimer [19]. We note that the C dimers of the first layer have a similar bond length in the two reconstructions (1.36 and 1.37 Å in the DR and SD, respectively), very close to that of the dimers on the diamond (001) surface [20]. In both geometries the Si-C distance between the first and second layers is sensibly longer than its bulk value ($\simeq 5\%$). However, in the SD reconstruction only the first C layer shows important deviations from the ideal geometry, whereas in the DR reconstruction several layers take part in the reconstruction with, e.g., the third layer having a large buckling (0.37 Å).

To investigate whether a C-SiC(001) surface can exhibit an SD and/or DR reconstruction in the temperature regime where Si desorption occurs, we studied the thermal stability of the SD and DR geometries. In our calculations the SD geometry is stable against thermal fluctuations up to 1200 K. At this temperature the distance between the first and second layer becomes considerably larger than at $T = 0$. Eventually some of the Si-C bonds break, yielding C dimers bonded only at one end to two Si atoms of the second layer. After some oscillations these dimers rotate by about 90° and are finally bonded to Si atoms at both ends with one bond per C atom. Si atoms in the second layer form dimers. We call such a configuration a bridge (B) pattern (see Fig. 1). We also obtained a B reconstruction by deposition of C dimers on a Si-SiC(001) surface, as we will discuss below. Our simulations clearly show that an SD geometry can transform to a B geometry at high temperature, whereas no tendency to form DR configurations was observed within the spanned temperature range.

When heating the DR reconstruction up to 1800 K we did not observe any topological change of the surface in spite of a considerable elongation and occasional breaking of the Si-C bonds between the uppermost layers. The C dimers mostly oscillate in the surface plane. Dimerization of some Si atoms in the second layer was observed above 1200 K. In the DR geometry, 90° dimer rotations that could give rise to B configurations are less favored than in the SD geometry; only a collective motion of all the dimers could allow such a structural transition.

In summary, depending on initial conditions, an ideally terminated C-SiC(001) surface at finite temperature can spontaneously reconstruct into two different geometries,

which are both stable up to the temperature range of Si sublimation experiments. Therefore the reconstruction resulting from Si desorption is expected to be determined by the kinetics of the sublimation process and the precise temperature at which Si removal occurs, rather than by the energetics of the surface at $T = 0$. Furthermore, we find that the coexistence of various reconstruction patterns, including DR, SD, and B geometries, is possible in the temperature range of sublimation experiments [21].

The photoemission data of Parrill *et al.* [6] for Si sublimated surfaces did not reveal the presence of any Si-Si bonds, which would instead be present in a B geometry. This is consistent with our simulations at $T \leq 1200$ K. Our results are also consistent with the data of Semond *et al.* [9], who obtained rather inhomogeneous surfaces by thermal desorption. However, there is so far no experimental evidence of $p(2 \times 1)$ reconstructions resulting from Si sublimation. This could be explained either by the kinetics of the Si desorption process or by entropic effects at high temperature, which may favor $c(2 \times 2)$ reconstructions.

In order to make contact with experiments preparing C-SiC(001) surfaces by ethylene deposition on Si-SiC(001) substrates, we performed a second series of computations. We arranged C dimers in a staggered pattern on an ideally Si-terminated surface and optimized the geometry of the system. The dimers were given two inequivalent (perpendicular) orientations on the top and on the bottom surfaces. After annealing, a B reconstruction was obtained on both faces: the top C dimers rearranged so as to induce a marked dimerization of the second layer Si atoms. The bottom C dimers turned by 90° to yield eventually the same geometrical pattern as on the top surface. We obtain a remarkably small (1.23 Å) C-C distance in the C dimers, indicating triple bonds, and a bond length of the Si dimers (2.37 Å) similar to that in bulk Si (2.35 Å). Contrary to what is found in the SD and DR reconstructions, the Si-C distance between the uppermost layers decreases by about 3% with respect to its bulk value. As in the DR geometry, several layers take part in the reconstruction.

The calculated total energy of the B reconstruction is lower than that of the SD by 0.18 eV/dimer and higher than that of the DR by 0.2 eV/dimer. These results agree well with those of Sabisch *et al.* [15], although our energy differences are larger than in their calculations and are consistent with the findings of Ref. [14]. Also our results for the surface geometries at $T = 0$ are in general good agreement with those of Ref. [14,15].

Our simulations, showing that C_2 molecules deposited on a Si-SiC(001) surface can yield a stable B reconstruction, confirm the experimental results of Long *et al.* [11], who recently demonstrated that C_2H_4 deposition on Si-SiC(001) leads to a B geometry. It would be very interesting to explore whether other hydrocarbons (containing, e.g., twofold coordinated C atoms) might lead to the so far unobserved DR reconstruction. Powers *et al.* [5] also reported that ethylene deposition on Si-SiC(001) leads to a

B geometry. However, they suggested that Si desorption should yield as well a B reconstruction in spite of difficulties encountered in fitting either an SD or a B geometry to their data for Si sublimated surfaces. These difficulties can be understood in view of our results, by a possible coexistence of SD and B configurations in surfaces prepared by Si desorption.

We now turn to the discussion of the electronic properties of the C-SiC(001) surfaces and in particular of surface band structures (SBS). In the B reconstruction the valence band top (VBT), located at $\overline{\Gamma}$, has a clear bulk character, whereas in other parts of the SBZ the highest occupied state has a surface character. This surface state is a combination of σ bonding orbitals on the Si dimers and of π_z bonding orbitals on the C dimers. The conduction band bottom (CBB) (also at $\overline{\Gamma}$) has again bulk character. Above the CBB we found two surface-bulk resonances. The lowest in energy has large components on the C dimers, given by antibonding combinations of p_x orbitals, which are orthogonal to the dimer orientation (π_x^* state). At the SBZ boundaries a surface state with antibonding p_z components on C dimers was observed (p_z^* state). These results are in very good agreement with the spectra of Long *et al.* [11] which show a prominent p_z peak with surface character and a less intense π_x state at higher energies [22]. As pointed out in Ref. [11] the existence of a π_x state is a clear signature of the B reconstruction. Furthermore, Long *et al.* found evidence of states coming from Si-Si bonds from Si 2p CLS measurements. In our calculation the B structure is semiconducting with a gap of $\simeq 1.4$ eV.

The SBS of the SD and DR geometries are simpler than that of the B reconstruction due to the absence of Si-Si bonds. In both surfaces the highest occupied (HO) and lowest unoccupied (LU) states at the $\overline{\Gamma}$ point have bulk character. Close to the VBT and CBB, three surface states were observed: a π_z, a π_y^*, and a π_z^* state, localized on the C dimers [23]. Our SBS results agree very well with those reported by Sabisch *et al.* [15].

In order to predict the results of STM experiments for the C-SiC(001) surfaces we report in Fig. 2 the square moduli of the HO and LU surface states for the three geometries, on a plane parallel to the surface at a distance of 1.5 Å. There is an unequivocal difference between the images of the $p(2 \times 1)$ and the $c(2 \times 2)$ surfaces. Drawing a clear distinction between the B and SD images is more delicate. When rotated by 90° the images of the π_x^* and π_z states of the B surface may not be clearly distinguishable from those of the π_y^* and π_z^* of the SD surface. The key difference between the two sets of images lies in the state occupation: The π states perpendicular to the surface are occupied (empty) and those parallel to the surface are empty (occupied) in the B (SD) geometry. Figure 2 suggests that STM experiments could be effective probes to identify the various reconstructions and possibly reveal the coexistence of domains with different reconstructions on the same surface, as was recently observed in diamond (001) [24].
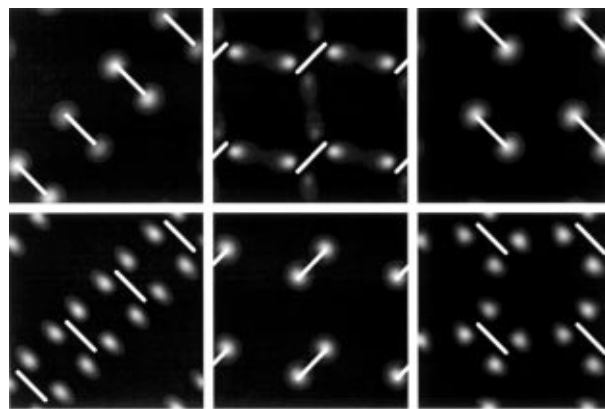
FIG. 2. Square moduli of the highest occupied (lower panel) and lowest unoccupied (upper panel) surface states in a plane parallel to the surface, at a distance of 1.5 Å, for the DR (left, π_y^* and π_z^* states), the B (center, π_z and π_x^* states), and the SD (right, π_y^* and π_z^* states) reconstructions of the C-SiC(001) surface (see Fig. 1). White bars indicate C dimers. In the B reconstruction, at 1.5 Å from the surface the electronic states are dominated by C dimers components and Si dimers components are not visible.

We further analyzed the differences between the reconstructions of C-SiC(001) by computing Si-2p and C-1s core level shifts with respect to bulk SiC. We adopted the procedure of Ref. [25] and ionized atoms of the two uppermost layers [26]. The values obtained for Si-2p CLS in the SD and DR reconstructions are similar (-0.12 and -0.09 eV), but different in magnitude and sign from that calculated for the B reconstruction (0.32 eV). Indeed Si-Si bonds exist only in the B geometry. C-1s CLS of the atoms of the first layer are instead very similar in the three structures (-0.44, -0.48, and -0.46 eV for the SD, DR, and B geometries, respectively), although only in the B reconstruction C dimers are triply bonded. Our calculated C-1s CLS for the B geometry is smaller than the experimental value [11] (-1.1 eV), the error being close to that found in a variety of carbon systems [27]. Whereas the LDA is believed to give a good quantitative description of CLS involving Si atoms [25], only a qualitative agreement between theory and experiment is obtained for CLS of several C systems [27]. For the B geometry we also computed the CLS of C atoms of inner layers. These CLS have magnitudes similar to those of the uppermost C atoms but have opposite signs. We therefore expect the presence of broad peaks in C-1s core absorption data.

Si-terminated surfaces.—In our calculations for Si-SiC(001), in the ground state geometry at $T = 0$ the surface shows a tendency to form a $p(2 \times 1)$ dimer row reconstruction, which lies a few meV/atom lower than the ideal surface geometry. However, the Si dimer bond length (d_{Si}), 2.58 Å, is much larger than, e.g., the bond length of the dimers on the Si(001) surface (2.26 Å) [28], and than the value (2.31 Å) fitted to LEED data [7]. We investigated the thermal stability of the reconstructed surface by performing constant temperature MD simulations in the range $200 \leq T \leq 800$ K. At

$T \simeq 300$ K the surface dimer length varies between $\simeq 2.3$ and 2.9 Å, i.e., close to the value of the ideal structure (3.03 Å). At higher temperatures ($300 \leq T \leq 500$ K) the surface oscillates between a $p(2 \times 1)$ dimer row reconstruction and an ideal surface geometry. The large thermal fluctuations of d_{Si} could be responsible for the difficulties encountered in achieving a good fit of LEED data for Si-SiC(001) surfaces [3,7,10]. At $T \geq 500$ K, we observed a tendency to form a $c(4 \times 2)$ reconstruction, where neighboring dimers have opposite buckling [29]. The ability of the Si-SiC(001) surface to sample several reconstructions in a relatively small temperature range could explain the differences between recent [10] and older LEED experiments [3,7]. Finally, we evaluated Si-$2p$ CLS and found a value (0.85 eV) which is in very good agreement with experiment (0.8–1.0 eV) [10].

In summary, we investigated the effect of preparation conditions on C-terminated β-SiC (001) surfaces, as well as the thermal stability of both C-terminated and Si-terminated surfaces. Computations of band structures and C-$1s$ and Si-$2p$ core level shifts of the stable C-SiC(001) geometries point at STM images and Si-$2p$ CLS as effective probes to identify the different reconstructions.

Note added.—An extremely weak (1×2) LEED pattern for C-terminated surfaces was indeed observed in Ref. [4] at submonolayer coverage. Thus patches of (1×2) domains on otherwise $c(2 \times 2)$ surfaces cannot be ruled out. We thank V. Bermudez for pointing this out.

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[19] Total energy differences obtained with the 11 and 19 layer slabs differ by $\simeq 0.03$ eV/dimer; for surface states, eigenvalue differences are very similar, whereas for bulk states they can differ by as much as 0.5 eV.

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[22] In our calculation the energy ordering of the p_z and π_x states differs from experiment. This is partly due to size effects [19] and partly to the LDA, since self-energy corrections can be of different magnitudes on localized and extended states [see, e.g., X. Blase, X. Zhu, and S. Louie, Phys. Rev. B **49**, 4973 (1994)].

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